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(54) Conductive paste compound for via hole filling, printed circuit board which uses the conductive paste, and method of manufacturing the same.

(57) A conductive paste compound for via hole filling includes a conductive filler at 80 to 92 weight percent with an average particle size of from 0.5 to 20 μm and specific surface of from 0.1 to 1.5 m^2/g , a liquid epoxy resin at 4.5 to 20 weight percent containing 2 or more epoxy groups with room temperature viscosity of 15 Pa·sec or less, and a hardener at 0.5 to 5 weight percent, wherein the viscosity is 2,000 Pa·sec or less and the volatile amount is 2.0 weight percent or less. A filling paste and a printed circuit board with use thereof are provided which can conduct an inner-via-hole connection between electrode layers without using a through-hole plating technique.

The conductive paste comprises a metallic particle 103 such as copper, an epoxy resin, a hardener, and if necessary, a dispersant. The paste having low viscosity and low volatility under high shear is used to fill holes disposed in a laminated substrate 101. Then, this substrate is heated and pressurized together with copper foil

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102 on both sides to attain a printed circuit board where both sides are electrically inner-via-hole connecte

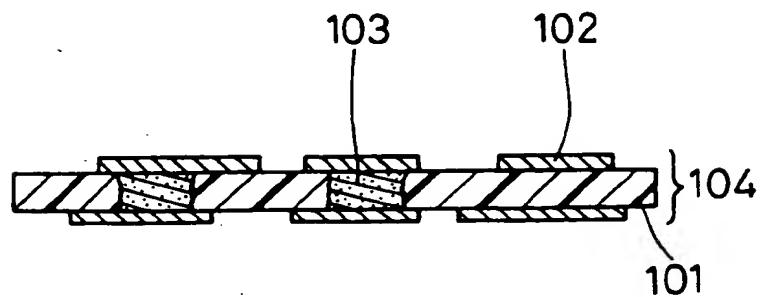


FIG.1

This invention relates to a conductive paste compound used for filling via holes and further relates to a double sided printed circuit board and a multilayer printed circuit board which uses the conductive paste.

Recently, following the tendency of electronic devices towards high performance and compact size, a circuit board is required to have a high degree of lamination and high density. As a method of connecting 5 layers within a substrate which can bond integrated circuits (IC) and components at the shortest distance, it is well-known that higher density can be attained through an inner-via-hole connection. In the case of a through-hole connection employed for a typical glass epoxy multilayer substrate, the connection is achieved by plating through-holes so that it was difficult to connect only the necessary layers. In addition, since the substrate comprises a top layer having an electrode land, this part can not be used to construct an 10 electrode land of a surface mounting part. Therefore, due to these restrictions, the mounting density can not be easily enhanced.

In order to solve these problems, methods other than using through-holes are employed, for example, a method of reducing through-holes by disposing holes halfway in a substrate, or a method of improving 15 mounting density by filling conductive paste in through-holes and by further closing up holes disposed in the top layer of a substrate at a plating step. However, due to the complicated manufacturing processes, the above-mentioned methods have cost and quantity production problems. On the other hand, simply the necessary layers can be connected in the inner-via-hole connection, and since there is no through-holes in the top layer of the substrate, the mounting property is also excellent.

When this connecting method is applied to a resin substrate, e.g. to a glass epoxy substrate, a double 20 sided substrate establishes continuity by filling up through-holes with low-viscous solvent-type silver paste by means of a printing method and then dried and hardened. However, the specific resistance value of this connection is as high as about $10^{-3} \Omega \cdot \text{cm}$, and the reliability in heat and shock resistance such as in the heat cycle is poor.

In order to reduce the viscosity of conductive paste, conventional methods employed were to use large 25 particles for reducing the amount of conductive filler or specific surface area, or to add a solvent with a low boiling point or a reactant type diluent.

However, when an additive amount of conductive filler was reduced, or when large particles were used, the problem occurred that contact points between fillers decreased and the resistance value of a via-hole-connection became so high that reliability could not be maintained in a test where thermal stress occurs, 30 e.g., in the heat cycle test.

With use of the method in which a solvent with a low boiling point or a reactant type diluent was added, these components volatilized and decreased enormously in weight while being hardened through heat-pressing. Due to these volatile components, the base material either swelled or lost peel strength to the copper foils of the wiring.

35 Furthermore, when a dispersant was not added, it was a problem that particle forms were limited to reduce viscosity, and that a printed filling of via holes was difficult even with use of those which are rather low in viscosity since the viscosity raised under high shear during the printing process.

An object of this invention is to solve the above-noted problems by providing a conductive paste 40 compound having low viscosity and low volatility which can achieve an electrical connection and heat and shock resistance between electrode layers through an inner-via-hole connection. Another object of this invention is to provide a double sided printed circuit board up to a multilayer printed circuit board including inner-via-hole connections using this paste.

In order to accomplish these and other objects and advantages, a conductive paste compound used for 45 filling via holes of this invention comprises (a) a conductive filler in an amount of 80 to 92 weight percent, having an average particle size of 0.5 to 20 μm and a specific surface area of 0.1 to 1.5 m^2/g , (b) a liquid epoxy resin in an amount of 4.5 to 20 weight percent, containing two or more epoxy groups and having a room temperature viscosity of 15 $\text{Pa}\cdot\text{sec}$ or less, and (c) a hardener in an amount of 0.5 to 5 weight percent, wherein the viscosity of the conductive paste compound is 2,000 $\text{Pa}\cdot\text{sec}$ or less and the amount of volatile components is 2.0 weight percent or less.

50 It is preferable that the conductive paste compound used for filling via holes further comprises a dispersant at 0.01 to 1.5 weight percent against 100 weight parts of the components (a) to (c).

Furthermore, it is preferable that the conductive filler comprises at least one fine grain selected from the group consisting of gold, silver, palladium, copper, nickel, tin, and lead. It is preferable that the fine grain has a diameter of from 0.5 to 20 μm .

55 It is also preferable that the conductive filler comprises copper with a surface oxygen concentration of 1.0 weight percent or less.

In addition, it is preferable that the epoxy resin comprises at least one-component liquid epoxy resin selected from the group consisting of bisphenol A epoxy resin, bisphenol F epoxy resin, alicyclic epoxy

resin, amine epoxy resin, and glycidyl esterified epoxy resin.

It is preferable that the liquid epoxy resin comprises 10 weight percent or more of an epoxy resin composed of glycidyl esterified dimer acids.

Furthermore, it is preferable that the liquid epoxy resin is a compound comprising at least 50 weight

5 percent or less of one epoxy resin selected from the group consisting of bisphenol A and bisphenol F, and further comprising 50 weight percent or more of epoxy resin composed of glycidyl esterified dimer acids with an epoxy equivalent of from 300 to 600 (g/eq).

10 It is also preferable that the hardener is at least one hardener selected from the group consisting of amine hardeners such as dicyandiamide and carboxylic acid hydrazide, urea hardeners such as 3-(3,4-dichlorophenyl)-1,1-dimethyl urea, acid anhydride hardeners such as phthalic acid anhydride, methynadic anhydride, phromellitic acid anhydride, hexahydro phthalic acid anhydride, and aromatic amine (amine adduct) hardeners such as diamide diphenylmethane, diamide diphenylsulfonic acid.

15 In addition, it is preferable that the hardener comprises a subclinical hardener.

It is preferable that the dispersant comprises at least one dispersant selected from the group consisting

15 of nonionic dispersants, e.g., ethylene oxide of higher fatty acid, propylene oxide addition ester compound, sorbitan fatty acid ester compound, ethylene oxide of polyhydric alcohol such as sorbitan, propylene oxide addition ether compound, ethylene oxide of alkylbenzene, propylene oxide additive, anionic dispersants, e.g., alkylbenzene sulfonic acid alkali salt, higher alcohol sulfate alkali salt, phosphate compound, higher fatty acid, ethylene oxide of higher fatty acid, propylene oxide additive such as sulfate alkali salt, and a

20 fourth class ammonium salt type cationic dispersant.

25 Next, a double sided printed circuit board of this invention comprises an insulating base material disposed with inner via holes which are filled with a conductive resin compound comprising a conductive filler in an amount of 80 to 92 weight percent and having an average particle size of 0.5 to 20 μ m and a specific surface area of 0.1 to 1.5 m²/g, and further comprising epoxy resin with an epoxy ring-opening in an amount of 4.5 to 20 weight percent, wherein the upper and lower electrode layers on the surface of the

insulating base material are electrically connected.

It is preferable that the insulating base material comprises a composite material of an aramid fiber and a thermosetting resin.

Furthermore, it is preferable that the insulating base material comprises a composite material of an aramid nonwoven fabric and an epoxy resin.

30 Next, a multilayer printed circuit board of this invention comprises a plurality of insulating base material layers and two or more electrode layers, wherein each insulating base material is disposed with inner via holes filled with a conductive resin compound comprising a conductive filler in an amount of 80 to 92 weight percent and having an average particle size of 0.5 to 20 μ m and a specific surface area of 0.1 to 1.5 m²/g, and further comprising an epoxy resin having an epoxy ring-opening in an amount of 4.5 to 20 weight percent, wherein each electrode layer is electrically connected.

It is preferable that the insulating base material comprises a composite material of an aramid fiber and a thermosetting resin.

Furthermore, it is preferable that the insulating base material comprises a composite material of an aramid nonwoven fabric and an epoxy resin.

40 A method of manufacturing a double sided printed circuit board of this invention comprises the steps of: disposing a prepreg used for manufacturing a printed circuit board with via holes in advance, filling the via holes with a conductive paste compound comprising (a) a conductive filler in an amount of 80 to 92 weight percent having an average particle size of 0.5 to 20 μ m and a specific surface area of 0.1 to 1.5 m²/g, (b) a liquid epoxy resin in an amount of 4.5 to 20 weight percent containing two or more epoxy groups and a room temperature viscosity of 15 Pa \cdot sec or less, and (c) a hardener in an amount of 0.5 to 5 weight percent, wherein the conductive paste compound has a viscosity of 2,000 Pa \cdot sec or less and the amount of volatile component is 2.0 weight percent or less, placing the prepreg between copper foils on the upper and lower layers and providing heat and pressurization, and forming circuits by etching the copper foils.

50 It is preferable that the prepreg comprises a composite material of an aramid fiber and a thermosetting resin.

Furthermore, it is preferable that the prepreg comprises a sheet composed of an aramid nonwoven fabric impregnated with a thermosetting epoxy resin.

55 A first method of manufacturing a multilayer printed circuit board of this invention comprises the steps of: disposing a prepreg used for manufacturing a printed circuit board with via holes in advance, filling the via holes with a conductive paste compound comprising (a) a conductive filler in an amount of 80 to 92 weight percent having an average particle size of 0.5 to 20 μ m and a specific surface area of 0.1 to 1.5 m²/g, (b) a liquid epoxy resin in an amount of 4.5 to 20 weight percent containing two or more epoxy

groups and having a room temperature viscosity of 15 Pa·sec or less, and (c) a hardener in an amount of 0.5 to 5 weight percent, wherein the viscosity is 2,000 Pa·sec or less and the amount of volatile component is 2.0 weight percent or less, positioning the prepreg above and below a double sided printed circuit board, placing the preprints between copper foils on the top layers, providing heat and pressurization, and etching the copper foils.

5 It is preferable that the prepreg comprises a composite material of an aramid fiber and a thermosetting resin.

Furthermore, it is preferable that the prepreg comprises a sheet composed of an aramid nonwoven fabric impregnated with a thermosetting epoxy resin.

10 A second method of manufacturing a multilayer printed circuit board of this invention comprises the steps of: disposing a prepreg used for manufacturing a printed circuit board with via holes in advance, filling the via holes with a conductive paste compound comprising (a) a conductive filler in an amount of 80 to 92 weight percent having an average particle size of 0.5 to 20 μm and a specific surface area of 0.1 to 1.5 m^2/g , (b) a liquid epoxy resin in an amount of 4.5 to 20 weight percent and containing two or more epoxy groups and having a room temperature viscosity of 15 Pa·sec or less, and (c) a hardener in an amount of 0.5 to 5 weight percent, wherein the conductive paste has a viscosity of 2,000 Pa·sec or less and an amount of volatile component is 2.0 weight percent or less, positioning the prepreg above and below a double sided printed circuit board, providing heat and pressurization, and forming circuits.

15 It is preferable that the prepreg comprises a composite material of an aramid fiber and a thermosetting resin.

20 Furthermore, it is preferable that the prepreg comprises a sheet composed of an aramid nonwoven fabric impregnated with a thermosetting epoxy resin.

25 According to the embodiments of this invention, a non-solvent one-component conductive compound can be obtained by dispersing a specific conductive filler within an epoxy resin having specific characteristics. Furthermore, by filling via holes with this conductive compound, a double sided printed circuit board and a multilayer printed circuit board can be obtained which have a highly reliable via-hole-connection.

30 First, the conductive filler will be explained. The conductive filler should preferably be contained in the conductive compound in high concentration. The reason for this is that, as mentioned above, conductive reliability must be maintained by raising the contact probability of the conductive fillers to each other even if the substrates are distorted due to lower resistance of connected via holes or due to thermal and mechanical stress.

35 In order to disperse the conductive filler with high concentration, the average particle size of the conductive filler should be preferably from 0.2 to 20 μm , and should also have as small a specific surface area as possible. A preferred value for the specific surface is from 0.1 to 1.5 m^2/g , and more preferably, from 0.1 to 1.0 m^2/g . The average diameter can be measured by using a microscopic method or a light scattering method. Noble metals such as gold, silver, and palladium, or base metals such as copper, nickel, tin, and lead are illustrative examples of the conductive fillers, and it is also possible to use two different kinds or more of these metals simultaneously. As long as the conductive filler has the characteristics mentioned above, it can be a spherical shape or a flaked form etc.

40 It is especially desirable to use copper powder as the conductive filler in view of migration control, economic supply, and price stability. But in general, copper powder is easily oxidized, and this oxidation of copper powder obstructs conductivity when it is used for filling via holes in this invention. Therefore, the oxygen concentration of the copper powder is preferably 1.0 weight % or less.

45 Next, an epoxy resin of specific characteristics will be explained. In order to form a non-solvent one-component conductive compound, it is basically necessary to use a liquid resin as the epoxy resin. For the dispersion of the above-mentioned conductive filler in high concentration, viscosity of the epoxy resin must be 15 Pa·sec or less. If an epoxy resin with viscosity higher than this value is used, viscosity of the conductive compound formed into paste becomes extremely high. This causes an inconvenience in that a via hole filling process can not take place when the paste viscosity of the conductive compound is 2,000 Pa·sec or higher. In addition, a preferred lower limit in viscosity of the epoxy resin is 0.2 Pa·sec.

50 On the other hand, when this compound is heat-compressed after being filled into the via holes, a volatile constituent in this compound should preferably be controlled to prevent the volatile constituent from vaporizing and causing voids within the via hole filling structure or to prevent the prepreg from separating. The volatile amount is preferably as small as possible, and the above-noted problems can be avoided when the amount is 2.0 weight % or less.

55 Examples of suitable epoxy resins are liquid epoxy resins including two or more epoxy radicals, for example, bisphenol A-type epoxy resin, bisphenol F-type epoxy resin, alicyclic epoxy resin, and amine epoxy resin. It is also possible to use liquid epoxy resin which are processed by molecular distillation to

reduce the volatile amount.

Above all, an epoxy resin composed of glycidyl esterified dimer acids has low viscosity (e.g. 0.2 to 0.9 Pa· sec). Also, a hardened substance of this epoxy resin shows flexibility, and its relaxation effect against stress is large. Therefore, when this epoxy resin is blended within the epoxy resin at 10 weight part 5 or more, reliability of the via hole structure becomes higher.

Here, it is preferable that the liquid epoxy resin is a compound comprising at least 50 weight % or less of one epoxy resin selected from the group consisting of bisphenol A and bisphenol F, and further comprising 50 weight % or more of epoxy resin composed of glycidyl esterified dimer acids with an epoxy equivalent of from 300 to 600 g/eq. As a result, reliability of the via hole structure becomes higher in 10 which the epoxy resin has lower viscosity, the hardened substance shows flexibility, and the relaxation effect against stress is large.

With regard to hardeners, any ordinary hardener can be used here. Generally used hardeners include amine-type hardeners such as dicyandiamide and carboxylic acid hydrazide, urea-type hardeners such as 3-(3,4-dichlorophenyl)-1,1-dimethyl urea, acid anhydride hardeners such as phthalic acid anhydride, 15 methynadic anhydride, phromellitic acid anhydride, hexahydro phthalic acid anhydride, and aromatic amine-type (amine adduct) hardeners such as diamide diphenylmethane, diamide diphenylsulfonic acid. Above all, it is preferable to use a solid-type subclinical hardener, particularly in view of stability and workability of the compound. The solid-type subclinical hardener functions as follows. First, several kinds of amine component and epoxy resin are reacted to some degree, grained as resin particles, and reactive radicals such as 20 amine are shut up in a three-dimensional structure of polymer. When this is blended with an epoxy resin, the particles react partially on the surface. However, the reaction stops at this point, and they can be preserved at room temperature for a long time without changing the characteristics. Then, the particles start to melt or dissolve when heated at a temperature higher than predetermined, and the shut-up reactive radicals show up and start to react all at once, thereby hardening quickly.

25 As for dispersants, any ordinary dispersant can be used. First, generally used dispersants include nonionic dispersants such as ethylene oxide of higher fatty acid, propylene oxide addition ester compound, sorbitan fatty acid ester compound, ethylene oxide of polyhydric alcohol such as sorbitan, propylene oxide addition ether compound, ethylene oxide of alkylbenzene, propylene oxide additive etc. Secondly, anionic dispersants, e.g., alkylbenzene sulfonic acid alkali salt, higher alcohol sulfuric ester alkali salt, phosphate 30 compound, higher fatty acid, ethylene oxide of higher fatty acid, and sulfate alkali salt with propylene oxide additive can be used. Thirdly, a fourth class ammonium salt type cationic dispersant can be used.

In this instance, the dispersant is effective in reducing viscosity of the paste and adding fluidity to the metallic particles when shear is provided through increasing affinity between the metallic particle surface and an organic resin blended as binder in the paste. This function is seen in that the paste viscosity does 35 not increase even under high shear in a screen printing process, and the paste can be filled easily into via holes disposed on a substrate.

With regard to the prepreg, almost any substance can be used which is pressed to become thinner than the prepreg when hardened, e.g., glass epoxy, paper phenol, aramid epoxy etc.

According to the above-mentioned methods of this invention, it is possible to obtain a conductive past 40 compound for via hole filling which has low viscosity and low volatility. Also, a double sided printed circuit board and a multilayer printed circuit board can be formed easily which have excellent reliability containing inner-via-hole connections. Here, the inner-via-hole connection is a method of obtaining connection between layers of the double sided and multilayer printed circuit board at any optional position.

FIG. 1 is a cross-sectional view showing a structure of a double sided printed circuit board of an 45 embodiment of this invention.

FIG. 2 (a) - (d) are cross-sectional views showing a method of manufacturing a double sided printed circuit board of an embodiment of this invention.

FIG. 3 (a) and (b) are cross-sectional views showing a method of manufacturing a multilayer printed circuit board of an embodiment of this invention.

50 FIG. 4 (a) and (b) are cross-sectional views showing a method of manufacturing a multilayer printed circuit board of another embodiment of this invention.

FIG. 5 is a schematic view of a conductive particle used for a printed circuit board of an embodiment of this invention.

FIG. 6 is a graph showing the relationship between the change of via hole connection resistance value 55 in a heat cycle test and the frequency of the test in an embodiment of this invention, in which the via hole connection is achieved with paste containing each epoxy resin in a printed circuit board.

FIG. 7 is a graph showing the relationship between the change of via hole connection resistance value in a heat cycle test and the frequency of the test in an embodiment of this invention, in which the via hole

connection is achieved with paste containing epoxy resin with different mixing compositions in a printed circuit board.

FIG. 8 is a graph showing the relationship between the rotational frequency (shear) in an E-type viscometer and the viscosity of paste which includes a dispersant in different amounts.

5 This invention will be described by referring to the following illustrative examples and attached figures. In particular, the following embodiments refer to a double sided printed circuit board with use of a conductive paste for via hole filling, a method of manufacturing the same, and a multilayer printed circuit board with use thereof.

10 FIG. 1 is a cross-sectional view showing a structure of a double sided printed circuit board of an embodiment of this invention. A double sided printed circuit board 104 comprises a laminated base material 101, a copper foil 102 (In FIG. 1, a copper foil is formed into a circuit pattern), and a conductive via hole 103 in which a conductive paste has hardened. The major advantages of this invention are that a conductive paste compound can easily fill due to its low viscosity and low volatility, and that the substrate has excellent reliability since the connection is achieved by filling with a large amount of conductive filler. As laminated base material 101, it is possible to use laminated base materials which are widely known at present. Examples are a glass-epoxy base material, an aramid-epoxy base material, and a paper phenol base material. The base material is called "prepreg" before being heated and pressurized and comprises a glass cloth or a nonwoven fabric as a core material which is impregnated with an uncured resin.

15 As for the conductive filler, almost any kind of noble metals such as gold and silver or base metals such as copper, tin, nickel or lead can be used. In addition, not only pure metals can be used, but also alloyed metals or those comprising a metal or an insulating core covered with a conductive material as shown in FIG. 5. In FIG. 5, 501 denotes a spherical core, and 502 denotes a conductive material which covers the core surface and serves as the conductive filler.

20 FIG. 2 (a) to (d) are views showing a method of manufacturing a double sided printed circuit board of this invention. In FIG. 2, a laminated base material 201 is a prepreg. This prepreg is disposed with through-holes. Usually, a drill is used for this step, but a laser beam can be used for processing specific materials. FIG. 2 (b) shows a state in which FIG. 2 (a) is positioned between a copper foil 202. FIG. 2 (c) shows a state after FIG. 2 (b) is heated and pressurized. FIG. 2 (c) shows a state in which the through-holes disposed in the prepreg have an increased amount of metal filling after being heated and pressurized. Due to compression, the prepreg has become thinner and the resin has hardened. The conductive paste 203 remains compressed. Conductor 103 of this state serves for an electrical connection between the upper and lower sides. FIG. 2 (d) shows a state after copper foil 202 on the surface is processed (e.g., etched) into circuit patterns. Copper foil 102 becomes a circuit conductor after being processed. After that, printed circuit boards which are actually used must be processed further, for example, applied with a solder resist, printed with letters and signs, or disposed with holes for insert components.

25 FIGS. 3 (a) and (b) show a method of manufacturing a multilayer printed circuit board by repeatedly applying the above-mentioned method of manufacturing a double sided printed circuit board. FIG. 3 (a) shows a state in which a double sided circuit board 104 which serves as a core is positioned between substrates of FIG. 2 (a) having through-holes filled with conductive paste on both side (upper and lower sides) to which are further applied copper foil 202. When heated and pressurized from the upper and lower sides in this state, a multilayer printed circuit board of FIG. 3 (b) is obtained which has already established an inner-via-hole connection. When the copper foils on the upper and lower sides are patterned, a multilayer printed circuit board consisting of four layers is completed. After that, by repeating these steps, a multilayer printed circuit board with even more layers can be attained.

30 45 In the method of manufacturing the multi layer printed circuit board of FIG. 3, the double sided printed circuit board used for the core was the double sided printed circuit board of this invention. However, this is not necessarily the case here. Instead, it is clear that a conventional through-hole double sided printed circuit board can be applied as well. In this case, it is better to fill the through-holes in advance. Here, the through-hole substrate indicates a resin substrate, and not only can the through-hole substrate be used but also a ceramic substrate etc.

40 55 FIGS. 4 (a) and (b) show another method of manufacturing a multilayer printed circuit board. In FIG. 4 (a), a prepreg 201 which is filled with conductive paste 203 and is in the state before being heated and pressurized is positioned between two sheets of double sided printed circuit boards 104. When heated and pressurized in this state, a multilayer printed circuit board consisting of four layers of FIG. 4 (b) can be obtained. Not only a four-layer circuit board, but a multilayer printed circuit board consisting of more layers can be obtained by providing a plurality of double sided printed circuit boards, positioning the above-noted laminated substrates which is filled with a conductive filler and is in a state before being heated and pressurized between the double sided printed circuit boards, and heating and pressurizing.

In the method of manufacturing the multilayer printed circuit board of FIG. 4, the double sided printed circuit board used was a double sided printed circuit board of this invention. However, this is not necessarily the case. Instead, a conventional through-hole double sided printed circuit board can be applied as well. In addition, not only can the through-hole substrate be used but also a ceramic substrate etc.

5 Epoxy resins used in the following embodiments are indicated below.

- (1) bisphenol A-type epoxy resin (EPICOAT 828 manufactured by Yuka Shell Epoxy Co., Ltd., epoxy equivalent 184 ~ 194 g/eq)
- (2) bisphenol F-type epoxy resin (EPICOAT 807 manufactured by Yuka Shell Epoxy Co., Ltd., epoxy equivalent 160 ~ 175 g/eq)
- 10 (3) alicyclic epoxy resin (ST-1000 manufactured by Toho Kasei Co., Ltd., epoxy equivalent 200 ~ 220 g/eq)
- (4) amine-type epoxy resin (ELN-125 manufactured by Sumitomo Chemical Co., Ltd., epoxy equivalent 110 ~ 130 g/eq)
- 15 (5) epoxy resin composed of glycidyl esterified dimer acids (epoxy equivalent 390 ~ 470 g/eq). This resin is also called glycidyl ester type epoxy resin in these embodiments. This formula is shown as Formula 1 shown below.

Formula 1

20

25

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35

40

Example 1

In a first embodiment of this invention shown in FIG. 1, a prepreg was an aramid epoxy sheet (TA-01 manufactured by Teijin Ltd.) of 200 μ m in thickness. This prepreg was applied on one side with a 20 μ m thick polyethylene terephthalate film by an adhesive and was disposed with through-holes of 0.2 mm in diameter by a drill.

45 These through-holes were filled with via hole filling paste comprising a metal particle of silver, gold, copper, and nickel in a spherical and flake form at 85 weight percent, a resin composition of bisphenol A-type epoxy resin (EPICOAT 828 manufactured by Yuka Shell Epoxy Co., Ltd.) at 3 weight %, an epoxy resin composed of glycidyl esterified dimer acids (YD-171 manufactured by Toho Kasei Co., Ltd.) at 9 weight %, and a hardener of amine adduct hardener (MY-24 manufactured by Ajinomoto Co., Ltd.) at 3 weight %. They were mixed and kneaded in three roles. Table 1 shows the form of the metal particle, the average size of the particle, the specific surface area, and the viscosity of the via hole filling paste of 0.5 rpm in an E-type viscometer at room temperature.

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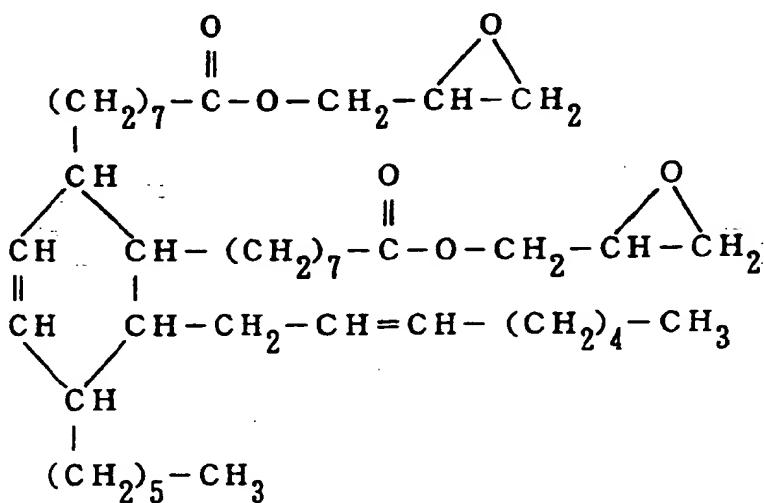


Table 1

Example	Powder	Form	Average size of particle μm	Specific surface area m^2/g	Paste viscosity Pa·sec	Via resistance $\times 10^{-5} \Omega \text{ cm}$
*1	silver	spherical	0.2	3.14	2,300	6.3
2			0.5	1.35	1,050	1.2
3			1.0	0.62	620	0.3
4			2.0	0.30	480	0.3
5			5.0	0.16	320	0.4
6			10.0	0.10	100	0.6
7		flake	20.0	0.13	120	1.5
*8			30.0	0.07	40	9.3
9	gold	spherical	2.0	0.40	650	0.3
10	copper	spherical	1.0	0.66	870	0.5
11			2.0	0.35	500	0.4
12			3.0	0.26	350	0.4
13		flake	10.0	0.20	400	1.5
14	nickel	flake	5.0	0.32	680	2.7

*: a comparative example

35 The prepeg filled with the paste was applied with copper foil 102 of $30\mu\text{m}$ thick on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurising 60 minutes at a temperature of 180°C and 50 Kg/cm^2 by heat-pressing.

When the paste viscosity was 2,000 Pa·sec or more, the filling in via holes was difficult to conduct due to high viscosity.

40 The double sided copper applied plate formed in this manner was formed into electrode patterns by using a conventional etching technique.

45 Table 1 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. In all cases, a low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin. The specific resistance value of each metal is silver ($1.6 \times 10^{-6} \Omega \text{ cm}$), gold ($2.3 \times 10^{-6} \Omega \text{ cm}$), and nickel ($6.8 \times 10^{-6} \Omega \text{ cm}$).

Example 2

50 As in the first embodiment, the prepeg of a second embodiment had through-holes formed with 0.2 mm in diameter, and these through-holes were filled with conductive paste comprising a metal particle of $2\mu\text{m}$ at 85 weight %, a resin selected from bisphenol A-type epoxy resin (EPICOAT 828 manufactured by Yuka Shell Epoxy Co., Ltd.), bisphenol F-type epoxy resin (EPICOAT 807 manufactured by Yuka Shell Epoxy Co., Ltd.), alicyclic epoxy resin (ST-1000 manufactured by Tohco Kasei Co., Ltd.), amine-type epoxy resin (ELN-125 manufactured by Sumitomo Chemical Co., Ltd.), and epoxy resin composed of glycidyl esterified dimer acids at 12 weight %, a hardener of amine adduct hardener (PN-23 manufactured by Ajinomoto Co., Ltd.) at 3 weight %. They were mixed and added in three roles. Table 2 shows the viscosity of the via hole filling paste at room temperature, the

decrease of the paste weight when heated to 300°C at a rate of 10°C/min., and the volatile amount. In all cases, the volatile amount was 2 weight % or less, and there was no swelling found during the substrate formation.

Table 2

Example	Resin	Paste viscosity Pa·sec	Volatile amount WT%	Via resistance $\times 10^{-5} \Omega$ cm
1	bisphenol A-type	1,500	0.16	0.4
2	bisphenol F-type	800	0.15	0.4
3	alicyclic epoxy	200	0.30	0.7
4	amine-type epoxy	60	0.30	0.6
5	glycidyl ester type	80	0.40	0.4

The prepreg having holes was filled with the paste and copper foil 102 was applied on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurizing 60 minutes at 180°C and 50 Kg/cm² by heat-pressing. Electrode patterns were formed by using a conventional etching technique.

Table 2 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. In all cases, a low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin.

Furthermore, FIG. 6 shows the change of the via hole connection resistance value in a heat cycle test (-55°C ~ 125°C, 30 minutes each) up to 1000 cycles.

The change of the via hole resistance value in each paste sample was 10 percent or less against the initial resistance value, so the reliability of the via hole was not ruined. In particular, the glycidyl ester type showed a rate of change at 1% or less. Due to the flexibility of the resin, only a slight change occurred against a thermal shock, and the reliability of the via-hole-connection was extremely good.

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Example 3

As in the first embodiment, the prepreg of a third embodiment had through-holes formed with 0.2 mm in diameter, and these through-holes were filled with conductive paste comprising a metal particle of copper powder with an average particle size of 2μm at 85 weight %, a blended resin consisting of Group A (bisphenol A-type epoxy resin, bisphenol F-type epoxy resin) and Group B (alicyclic epoxy resin, amine-type epoxy resin, or epoxy resin composed of glycidyl esterified dimer acids) at 12 gross weight %, and a hardener of amine adduct hardener (MY-24) at 3 weight %. They were mixed and kneaded in three roles. Table 3 shows the viscosity of the via hole filling paste of 0.5 rpm in an E-type viscometer at room temperature.

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Table 3

Example	Resin A	WT%	Resin B	WT%	Paste viscosity Pa·sec	Via resistance $\times 10^{-5} \Omega \text{ cm}$
1	bisphenol A-type	50	alicyclic	50	720	0.8
2		50	amine-type	50	540	0.6
3		75	glycidyl ester	25	1,060	0.5
5		50		50	660	0.5
6		25		75	380	0.4
7	bisphenol F-type	75	glycidyl ester	25	620	0.5
9		50		50	400	0.4
10		25		75	220	0.4

The prepreg filled with this paste was applied with copper foil 102 on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurising 60 minutes at 180 °C and 50 Kg/cm² by heat-pressing. Electrode patterns were formed by using a conventional etching technique.

Table 3 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. In all cases, a low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin.

Furthermore, FIG. 7 shows the change of the via hole resistance value in a heat cycle test (-55 °C ~ 125 °C, 30 minutes each) up to 1000 cycles.

The change of the via hole resistance value in each paste sample was 10 percent or less against the initial resistance value, so the reliability of the via hole was not ruined. In particular, the glycidyl ester mixed type showed a rate of change at 1 % or less at the amount content of 50 weight % or more, thereby maintaining the reliability of the via-hole-connection.

Example 4

As in the first embodiment, the prepreg of a fourth embodiment had through-holes formed with 0.2 mm in diameter, and these through-holes were filled with conductive paste comprising a metal particle of silver powder or copper powder with an average particle size of 2 μm at 75 to 92.5 weight %, a blended resin consisting of bisphenol A-type epoxy resin and epoxy resin composed of glycidyl esterified dimer acids in 25 to 75 weight ratio at 4.5 to 22 gross weight %, and a hardener of amine adduct hardener (MY-24) at 3 weight %. They were mixed and kneaded in three roles. Table 4 shows the viscosity of the via hole filling paste room temperature.

Table 4

Example	Metal weight WT%	Resin	WT%	Paste viscosity Pa·sec	Via resistance $\times 10^{-5} \Omega \text{ cm}$
1	silver 80.0	bisphenol A (25WT%) + glycidyl ester (75WT%)	17	250	0.7
2	85.0		12	480	0.4
*3	copper 75.0	bisphenol A (25WT%) + glycidyl ester (75WT%)	22	40	4.8
4	80.0		17	180	0.8
5	85.0		12	380	0.4
6	90.0		7	890	0.4
7	92.0		5	1,450	0.3
*8	92.5		4.5	2,310	0.3

*: a comparative example

The prepreg filled with this paste was applied with copper foil 102 on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurizing 60 minutes at 180°C and 50 Kg/cm² by heat-pressing. Electrode patterns were formed by using a conventional etching technique.

Table 4 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. In all cases, a low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin. On the other hand, when the metallic amount content was 80 weight % or less, the via hole resistance value was large due to the lack of the conductive metal. Furthermore, when the metallic amount content was 92 weight % or more, the via hole filling was difficult to conduct due to high paste viscosity.

Example 5

As in the first embodiment, the prepreg of a fifth embodiment had through-holes formed with 0.2 mm in diameter, and these through-holes were filled with conductive paste comprising a metal particle of silver powder or copper powder with an average particle size of 2μm at 85 weight %, a blended resin consisting of bisphenol A-type epoxy resin and epoxy resin composed of glycidyl esterified dimer acids in 25 to 75 weight ratio at 12 gross weight %, and dicyandiamide (DICY7 manufactured by Yuka Shell Epoxy Co., Ltd.) or acid anhydride (RIKACID MH manufactured by New Japan Chemical Co., Ltd.) or amine adduct hardener (PN-23, MY-24 manufactured by Ajinomoto Co., Ltd.) at 3 weight %. They were mixed and kneaded in three roles. Table 5 shows the viscosity of the via hole filling paste at room temperature and the volatile amount of the paste when heated to 300°C at a rate of 10°C/min.

Table 5

Example	Metal	Hardener	Paste viscosity Pa·sec	Volatile amount WT%	Via resistance $\times 10^{-5} \Omega \text{ cm}$
1	silver	dicyandiamide	520	0.32	0.4
2		acid anhydride	200	1.50	0.5
3		amine adduct(MY-24)	620	0.50	0.4
4		amine adduct(PN-23)	600	0.42	0.4
5	copper	dicyandiamide	380	0.35	0.4
6		acid anhydride	120	1.56	0.5
7		amine adduct(MY-24)	430	0.50	0.4
8		amine adduct(PN-23)	450	0.40	0.4

The prepreg filled with this paste was applied with copper foil 102 on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurizing 60 minutes at 180°C and 50 Kg/cm² by heat-pressing. Electrode patterns were formed by using a conventional etching technique.

Table 5 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. Regardless of the hardener type, a low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin.

Example 6

As in the first embodiment, the prepreg of a sixth embodiment had through-holes formed with 0.2 mm in diameter, and these through-holes were filled with conductive paste comprising a metal particle of copper powder with an average particle size of 2 μm at 85 weight %, a blended resin consisting of bisphenol A-type epoxy resin and epoxy resin composed of glycidyl esterified dimer acids in 25 to 75 weight ratio at 8 to 14.5 gross weight %, and phthalic anhydride or amine adduct type hardener (MY-24) at 0.5 to 7 weight %. They were mixed and kneaded and mixed in three roles. Table 6 shows the viscosity of the via hole filling paste at room temperature and the volatile amount of the paste when heated to 300°C at a rate of 10°C/min.

Table 6

Example	Hardener	Amount of hardener WT%	Paste viscosity Pa·sec	Volatile amount WT%	Via resistance $\times 10^{-5} \Omega \text{ cm}$
1	acid anhydride	0.5	160	0.60	0.8
2		3.0	120	1.56	0.5
3		5.0	120	1.95	0.4
*4		7.0	110	2.34	-
5	amine adduct	0.5	180	0.40	0.4
6		3.0	450	0.40	0.4
7		5.0	850	0.38	0.5
*8		7.0	2,400	0.35	20.0

*: a comparative example

The prepreg filled with this paste was applied with copper foil 102 on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurizing 60 minutes at 180 °C and 50 Kg/cm² by heat-pressing. Electrode patterns were formed by using a conventional etching technique.

Table 6 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. Regardless of the hardener type, a low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin. However, when too much solid powder such as an amine adduct hardener was added, the viscosity increased, so the via hole filling was difficult to conduct by using the paste added with a hardener of 5 weight % or more. Furthermore, when a hardener with high volatility such as acid anhydride had a volatile amount of more than 2 weight %, a double sided copper applied plate of satisfactory quality was not obtained due to swelling of the substrate and the electrode.

Example 7

As in the first embodiment, the prepreg of a seventh embodiment had through-holes formed with 0.2 mm in diameter, and these through-holes were filled with conductive paste comprising a metal particle of copper powder with an average particle size of 2 μm having different surface oxygen amounts at 85 weight %, a blended resin consisting of bisphenol A-type epoxy resin and epoxy resin composed of glycidyl esterified dimer acids in 25 to 75 weight ratio at 12 gross weight %, and a hardener of amine adduct hardener (MY-24) at 3 weight %. They were mixed and kneaded in three roles. Table 7 shows the viscosity of the via hole filling paste at room temperature.

Table 7

Example	Surface oxygen amount WT%	Paste viscosity Pa·sec	Via resistance $\times 10^{-5} \Omega$ cm
1	0.2	430	0.3
2	0.5	450	0.4
3	1.0	500	0.8
*4	1.2	680	2.5

*: a comparative example

5 The prepreg filled with this paste was applied with copper foil 102 on the upper and the lower sides.
 10 Then, this was formed into a double sided copper applied plate by heating and pressurizing 60 minutes at 180°C and 50 Kg/cm² by heat-pressing. Electrode patterns were formed by using a conventional etching technique.

15 Table 7 shows the resistance value of the inner-via-hole-connection conducted by using the respective
 20 paste. When using paste with the surface oxygen concentration of copper at 1.0 weight % or less, a low
 25 resistance connection was obtained in which the resistivity value was ten times or less of the specific
 30 resistance value of the conductor although the paste included an insulating resin. However, along with the
 35 increase in the surface oxygen concentration, the resistance of the inner-via-hole connection became
 40 higher. As soon as this amount exceeded 1.0 weight %, the resistance value increased radically. As a
 45 result, a low resistance connection was not obtained in which the resistivity value was ten times or less of
 50 the specific resistance value of the conductor.

Example 8

30 The conductive paste used here comprised a metal particle of copper powder with an average particle
 35 size of 2μm at 85 weight %, a blended resin consisting of bisphenol A-type epoxy resin and epoxy resin
 40 composed of glycidyl esterified dimer acids in 25 to 75 weight ratio at 12 gross weight %, and a
 45 hardener of amine adduct hardener (MY-24) at 3 weight % which had been kneaded and mixed in three
 50 roles. An aramid-epoxy prepreg comprised a prepreg disposed with through-holes of 0.2 mm in diameter
 55 which were filled with the above-mentioned paste. This aramid-epoxy prepreg was positioned between two
 60 sheets of aramidepoxy double sided substrates having patterns formed for the connection resistance
 measurement. Then, this was formed into a four-layer printed circuit board by heating and pressurizing 60
 65 minutes at 180°C and 50 Kg/cm² by heat-pressing.

70 The inner-via-hole connection resistance formed between the second and the third layer of the four-
 75 layer substrate showed the same resistance value as in the first embodiment. Also, a six-layer printed
 80 circuit board attained the same reliability with the same connection resistance value as in the four-layer
 85 printed circuit board.

90 Furthermore, the above-mentioned paste was used for manufacturing an aramid-epoxy double sided
 95 substrate with the same method as in Example 1. One sheet of this substrate was positioned between two
 100 sheets of aramid-epoxy preprints comprising preprints having through-holes of 0.2 mm in diameter filled
 105 with the above-noted paste. In the method of forming a four-layer printed circuit board by heating and
 110 pressurizing 60 minutes at 180°C and 50 Kg/cm² by heat-pressing, equivalent resistance was obtained for
 115 the via-hole-connection. In addition, the same reliability was obtained in a six-layer printed circuit board
 120 manufactured by using this method.

125 A ceramic substrate with circuits was used instead of the aramic-epoxy double sided substrate
 130 manufactured by the same method as in Example 1, and the same reliability was obtained for the via-hole-
 135 connection resistance.

Example 9

140 In a ninth embodiment of this invention shown in FIG. 1, the prepreg was an aramid-epoxy sheet (TA-01
 145 manufactured by Teijin Ltd.) of 200μm in thickness. This prepreg was applied on one side with a 20μm
 150 thick polyethylene terephthalate film by an adhesive and was disposed with through-holes of 0.2 mm in
 155 diameter by a drill.

These through-holes were filled with via hole filling paste comprising a metal particle of silver, gold, copper and nickel in a spherical and flake form at 85 weight %, a resin composition of bisphenol A-type epoxy resin (EPICOAT 828 manufactured by Yuka Shell Epoxy Co., Ltd.) at 3 weight %, an epoxy resin composed of glycidyl esterified dimer acids (YD-171 manufactured by Toho Kasei Co., Ltd.) at 9 weight %, a hardener of amine adduct hardener (MY-24 manufactured by Ajinomoto Co., Ltd.) at 3 weight %, and a dispersant at 0.01 to 2.0 weight % against the gross amount of the metal, the resin, and the hardener comprising polyoxyethylene sorbitan fatty acid ester (nonionic surface active agent "SOLGEN" TW manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.), phosphate (anion surface active agent "PLYSURF" manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.), and cation surface active agent "CATIOGEN" (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.). They were mixed and kneaded in three roles. Table 8 shows the form of the metal particle, the average size of the particle, the specific surface area, the type of the dispersant and its compounded amount (weight %), and the viscosity of the via hole filling paste of 0.5 rpm in an E-type viscometer at room temperature.

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Table 8

Example	Powder	Form	Average size of particle μ m	Specific surface area m ² /g	Dispersant Compounded amount at weight %	Paste viscosity Pa·sec	Via resistance x10 ⁻⁵ Ω cm
*1	silver	spherical	0.1	5.83	PLYSURF 0.20	2,350	4.7
2			0.2	3.14		1,620	1.2
3			0.5	1.35		850	0.4
4			1.0	0.62		480	0.3
5			2.0	0.30		390	0.3
6			5.0	0.16		270	0.4
7			10.0	0.10		80	0.6
8		flake	20.0	0.13		90	1.3
*9			30.0	0.07		30	10.3
10	gold	spherical	2.0	0.40		470	0.3
11	copper	spherical	1.0	0.66		820	0.5
*12			2.0	0.35	SOLGEN TW 0.20 CATIOGEN 0.20 PLYSURF 0.20	500	0.4
13						470	0.4
14						420	0.4
15						410	0.5
16						380	0.8
*17						350	2.3
18						450	0.4
19						460	0.4
20			3.0	0.26		300	0.4
21		flake	10.0	0.20		370	1.5
22	nickel	flake	5.0	0.32		610	2.0

*: a comparative example

The prepreg filled with the paste was applied with copper foil 102 of 35 μ m thick on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurizing 60 minutes at 180°C and 50 Kg/cm² by heat-pressing.

When the paste viscosity was 2,000 Pa•sec or more, which is beyond the limits of claims of this invention, the filling into via holes was difficult to conduct due to high viscosity.

The double sided copper applied plate formed in this manner was formed into electrode patterns by using a conventional etching technique.

Table 8 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. In all cases, a low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin. The specific resistance value of each metal used in this embodiment is silver ($1.6 \times 10^{-6} \Omega \text{ cm}$), gold ($2.3 \times 10^{-6} \Omega \text{ cm}$), copper ($1.7 \times 10^{-6} \Omega \text{ cm}$), and nickel ($6.8 \times 10^{-6} \Omega \text{ cm}$).

Furthermore, the change of the paste viscosity is shown in FIG. 8 in which shear is provided to the paste by changing the frequency with an E-type viscometer. It is desirable as filling paste that the viscosity decreases under high shear in a printing process rather than under the condition of no shear. The examples without dispersant added increased the viscosity when provided with shear, so it was difficult to fill the paste. On the other hand, the examples with dispersant added made a small increase in the viscosity under high shear, and for those added more than 0.5 weight part decreased the viscosity under high shear. Accordingly, the filling became easier to conduct. However, the examples with dispersant added 2.0 weight % or more had the connection of the metal particles disturbed, so the via connection resistance increased.

Example 10

As in the ninth embodiment, the prepreg of a tenth embodiment had through-holes formed with 0.2 mm in diameter, and these through-holes were filled with conductive paste comprising a metal particle of copper powder with an average size of 2 μ m at 85 weight %, a resin selected from bisphenol A-type epoxy resin, bisphenol F-type epoxy resin (EPICOAT 807 manufactured by Yuka Shell Epoxy Co., Ltd.), alicyclic epoxy resin (ST-1000 manufactured by Toho Kasei Co., Ltd.), amine type epoxy resin (ELN-125 manufactured by Sumitomo Chemical Co., Ltd.), and an epoxy resin composed of glycidyl esterified dimer acids at 12 weight %, a hardener of amine adduct hardener (PN-23 manufactured by Ajinomoto Co., Ltd.) at 3 weight %, and a dispersant of phosphate ("PLYSURF" manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) contained at 0.2 weight % against the gross amount of the metal, the resin, and the hardener. They were mixed and kneaded in three roles. Table 9 shows the viscosity of the via hole filling paste at room temperature and the decrease or the volatile amount of the paste when heated to 300°C at a rate of 10°C/min. In all cases, the volatile amount of the paste was 2 weight % or less, and there was no swelling found during the substrate manufacturing process.

Table 9

Example	Resin	Paste viscosity Pa•sec	Volatile amount WT%	Via resistance $\times 10^{-5} \Omega \text{ cm}$
1	bisphenol A-type	1,350	0.16	0.4
2	bisphenol F-type	720	0.15	0.4
3	alicyclic epoxy	180	0.30	0.8
4	amine-type epoxy	50	0.30	0.6
5	glycidyl ester type	60	0.40	0.6

The prepreg having holes was filled with the paste and applied with copper foil 102 on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurizing 60 minutes at 180°C and 50 Kg/cm² by heat-pressing. Electrode patterns were formed by using a conventional etching technique.

Table 9 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. In all cases, a low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin.

Example 11

As in the eighth embodiment, the prepreg of an eleventh embodiment had through-holes formed with 0.2 mm in diameter, and these through-holes were filled with conductive paste comprising a metal particle of copper powder with an average particle size of $2\mu\text{m}$ at 85 weight %, a blended resin consisting of Group A (bisphenol A-type epoxy resin, bisphenol F-type epoxy resin) and Group B (alicyclic epoxy resin, amine-type epoxy resin, epoxy resin composed of glycidyl esterified dimer acids) at 12 gross weight %, a hardener of amine adduct hardener (MY-24) at 3 weight %, and a dispersant of phosphate ("PLYSURF" manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) at 0.2 weight % against the gross amount of the metal, the resin, and the hardener. They were mixed and kneaded in three roles. An aramid-epoxy prepreg comprised a prepreg disposed with through-holes of 0.2 mm in diameter which were filled with the above-mentioned paste. Table 10 shows the viscosity of the via hole filling paste of 0.5 rpm in an E-type viscometer at room temperature.

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Table 10

Example	Resin A	WT%	Resin B	WT%	Paste viscosity Pa·sec	Via resistance $\times 10^{-5} \Omega \text{ cm}$
1	bisphenol A-type	50	alicyclic	50	650	0.8
2		50	amine-type	50	460	0.5
3		75	glycidyl ester	25	870	0.5
5		50		50	600	0.6
6		25		75	340	0.5
7	bisphenol F-type	75	glycidyl ester	25	570	0.5
9		50		50	380	0.4
10		25		75	200	0.5

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The prepreg filled with this paste was applied with copper foil 102 on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurizing 60 minutes at 180°C and 50 Kg/cm^2 by heat-pressing. Electrode patterns were formed by using a conventional etching technique.

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Table 10 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. A low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin.

Example 12

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As in the eighth embodiment, the prepreg of a twelfth embodiment had through-holes formed with 0.2 mm in diameter, and these through-holes were filled with conductive paste comprising a metal particle of silver powder or copper powder with an average particle size of $2\mu\text{m}$ at 75 to 92.5 weight %, a blended

resin consisting of bisphenol A-type epoxy resin and epoxy resin composed of glycidyl esterified dimer acids in 25 to 75 weight ratio at 4.5 to 22 gross weight %, a hardener of amine adduct hardener (MY-24) at 3 weight %, and a dispersant containing phosphate ("PLYSURF" manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) at 0.2 weight % against the gross amount of the metal, the resin, and the hardener. They were mixed and kneaded in three roles. Table 11 shows the viscosity of the via hole filling paste at room temperature.

Table 11

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Example	Metal weight WT%	Resin	WT%	Paste viscosity Pa·sec	Via resistance $\times 10^{-5} \Omega \text{ cm}$
1	silver 80.0	bisphenol A (25WT%) + glycidyl ester (75WT%)	17	250	0.7
2	85.0		12	480	0.4
*3	copper 75.0	bisphenol A (25WT%) + glycidyl ester (75WT%)	22	40	5.0
4	80.0		17	180	0.7
5	85.0		12	380	0.4
6	90.0		7	890	0.4
7	92.0		5	1,450	0.3
8	92.5		4.5	1,880	0.4
*9	93.0		4	2,680	—

*: a comparative example

The prepreg filled with this paste was applied with copper foil 102 on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurizing 60 minutes at 35 180°C and 50 Kg/cm² by heat-pressing. Electrode patterns were formed by using a conventional etching technique.

Table 11 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. A low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin. However, in the 40 compositions beyond the limits of claims of this invention, when the metallic amount content was 80 weight % or less, the via hole resistance value was large due to the lack of the conductive metal. Furthermore, when the metallic amount content was 92 weight % or more, the via hole filling was difficult to conduct due to high paste viscosity.

45 Example 13

As in the eighth embodiment, the prepreg of a thirteenth embodiment had through-holes formed with 0.2 mm in diameter, and these through-holes were filled with conductive paste comprising a metal particle of silver powder or copper powder with an average particle size of 2 μm at 85 weight %, a blended resin 50 consisting of bisphenol A-type epoxy resin and epoxy resin composed of glycidyl esterified dimer acids in 25 to 75 weight ratio at 12 gross weight %, a hardener of dicyandiamide (DICY7 manufactured by Yuka Shell Epoxy Co., Ltd.) or acid anhydride (RIKACID MH manufactured by New Japan Chemical Co., Ltd.) or 55 amine adduct hardener (PN-23, MY-24 manufactured by Ajinomoto Co., Ltd.) at 3 weight %, and a dispersant containing phosphate ("PLYSURF" manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) at 0.2 weight % against the gross amount of the metal, the resin, and the hardener. They were mixed and kneaded in three roles. Table 12 shows the viscosity of the via hole filling paste at room temperature (25°C) and the volatile amount of the paste when heated to 300°C at a rate of 10°C/min.

Table 12

Example	Metal	Hardener	Paste viscosity Pa·sec	Volatile amount WT%	Via resistance $\times 10^{-5} \Omega \text{ cm}$
1	silver	dicyandiamide	470	0.32	0.4
2		acid anhydride	180	1.50	0.4
3		amine adduct(MY-24)	540	0.50	0.4
4		amine adduct(PN-23)	520	0.42	0.4
5	copper	dicyandiamide	320	0.35	0.4
6		acid anhydride	100	1.56	0.5
7		amine adduct(MY-24)	380	0.50	0.4
8		amine adduct(PN-23)	380	0.40	0.4

The prepreg filled with this paste was applied with copper foil 102 on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurising 60 minutes at 180°C and 50 Kg/cm² by heat-pressing. Electrode patterns were formed by using a conventional etching technique.

Table 12 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. Regardless of the hardener type, a low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin.

Example 14

As in the eighth embodiment, the prepreg of a fourteenth embodiment had through-holes formed with 0.2 mm in diameter, and these through-holes were filled with conductive paste comprising a metal particle of silver powder or copper powder with an average particle size of 2μm at 85 weight %, a blended resin consisting of bisphenol A-type epoxy resin and epoxy resin composed of glycidyl esterified dimer acids in 25 to 75 weight ratio at 8 to 14.5 gross weight %, a hardener of phthalic anhydride or amine adduct hardener (MY-24) at 0.5 to 7 weight %, and a dispersant containing phosphate ("PLYSURF" manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) at 0.2 weight % against the gross amount of the metal, the resin, and the hardener. They were mixed and kneaded in three roles. Table 13 shows the viscosity of the via hole filling paste at room temperature and the volatile amount of the paste when heated to 300°C at a rate of 10°C/min.

Table 13

Example	Hardener	Amount of hardener WT%	Paste viscosity Pa·sec	Volatile amount WT%	Via resistance $\times 10^{-5} \Omega \text{ cm}$
1	acid anhydride	0.5	140	0.60	0.9
2		3.0	100	1.58	0.5
3		5.0	110	1.95	0.4
*4		7.0	110	2.34	-
5	amine adduct	0.5	170	0.40	0.5
6		3.0	410	0.40	0.5
7		5.0	720	0.38	0.5
*8		7.0	2,100	0.35	15.0

*: a comparative example

The prepreg filled with this paste was applied with copper foil 102 on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurizing 60 minutes at 180°C and 50 Kg/cm² by heat-pressing. Electrode patterns were formed by using a conventional etching technique.

Table 13 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. Regardless of the weight ratio of the hardener, a low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin. However, when too much solid powder such as an amine adduct hardener was added, the viscosity increased, so the via hole filling was difficult to conduct by using the paste added with a hardener of 5 weight % or more. Furthermore, when a hardener with high volatility such as acid anhydride had a volatile amount of more than 2 weight %, a double sided copper applied plate of satisfactory quality was not obtained due to swelling of the substrate and the electrode.

Example 15

As in the eighth embodiment, the prepreg of a fifteenth embodiment had through-holes formed with 0.2 mm in diameter, and these through-holes were filled with conductive paste comprising a metal particle of copper powder with an average particle size of 2 μm having different surface oxygen amounts at 85 weight %, a blended resin consisting of bisphenol A-type epoxy resin and epoxy resin composed of glycidyl esterified dimer acids in 25 to 75 weight ratio at 12 gross weight %, a hardener of amine adduct hardener (MY-24) at 3 weight %, and a dispersant containing phosphate ("PLYSURF" manufactured by Daiichi Kogyo Seiyaku Co., Ltd.) at 0.2 weight % against the gross amount of the metal, the resin, and the hardener. They were mixed and kneaded in three roles. Table 14 shows the viscosity of the via hole filling paste at room temperature.

Table 14

Example	Surface oxygen amount WT%	Paste viscosity Pa·sec	Via resistance $\times 10^{-5} \Omega$ cm
1	0.2	400	0.3
2	0.5	410	0.3
3	1.0	430	0.5
*4	1.2	580	2.5

*: a comparative example

The prepreg filled with this paste was applied with copper foil 102 on the upper and the lower sides. Then, this was formed into a double sided copper applied plate by heating and pressurizing 60 minutes at 180°C and 50 Kg/cm² by heat-pressing. Electrode patterns were formed by using a conventional etching technique.

Table 14 shows the resistance value of the inner-via-hole-connection conducted by using the respective paste. When using paste with the surface oxygen concentration of copper at 1.0 weight % or less, a low resistance connection was obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor although the paste included an insulating resin. However, along with the increase in the surface oxygen concentration, the resistance of the inner-via-hole connection became higher. As soon as this amount exceeded 1.0 weight %, the resistance value increased radically. As a result, a low resistance connection was not obtained in which the resistivity value was ten times or less of the specific resistance value of the conductor.

Example 16

Conductive paste used here comprised a metal particle of copper powder with an average particle size of 2 μ m at 85 weight %, a blended resin consisting of bisphenol A-type epoxy resin and epoxy resin composed of glycidyl esterified dimer acids in 25 to 75 weight ratio at 12 gross weight %, a hardener of amine adduct hardener (MY-24) at 3 weight %, and a dispersant containing phosphate ("PLYSURF" manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) at 0.2 weight % against the gross amount of the metal, the resin, and the hardener. They were mixed and kneaded in three roles. An aramid-epoxy prepreg comprised a prepreg disposed with through-holes of 0.2 mm in diameter which were filled with the above-mentioned paste. This aramid-epoxy prepreg was positioned between two sheets of aramid-epoxy double sided substrates having patterns formed for the connection resistance measurement. Then, this was formed into a four-layer printed circuit board by heating and pressurizing 60 minutes at 180°C and 50 Kg/cm² by heat-pressing.

The inner-via-hole connection resistance formed between the second and the third layer of the four-layer substrate showed the same resistance value as in the first embodiment. Also, a six-layer printed circuit board attained the same reliability with the same connection resistance value as in the four-layer printed circuit board.

Furthermore, the above-mentioned paste was used for manufacturing an aramid-epoxy double sided substrate with the same method as in Example 8. One sheet of this substrate was positioned between two sheets of aramid-epoxy preprints comprising preprints having through-holes of 0.2 mm in diameter filled with the above-noted paste. In the method of forming a four-layer printed circuit board by heating and pressurizing 60 minutes at 180°C and 50 Kg/cm² by heat-pressing, equivalent resistance was obtained for the via-hole-connection. In addition, the same reliability was obtained in a six-layer printed circuit board manufactured by using this method.

A ceramic substrate with circuits was used instead of the aramic-epoxy double sided substrate manufactured by the same method as in Example 8, and the same reliability was obtained for the via-hole-connection resistance.

As described above, according to a double sided printed circuit board, a multilayer printed circuit board, and methods of manufacturing the same with use of the via hole filling paste of this invention, a double sided printed circuit board with inner via holes can be attained without using a through-hole plating technique. Furthermore, this circuit board can be formed into a multilayer printed circuit board easily.

Claims

1. A conductive paste compound used for filling via holes comprising (a) a conductive filler in an amount of 80 to 92 weight percent having an average particle size of 0.5 to 20 μ m and a specific surface area of 0.1 to 1.5 m²/g, (b) a liquid epoxy resin in an amount of 4.5 to 20 weight percent containing two or more epoxy groups and having a room temperature viscosity of 15 Pa·sec or less, and (c) a hardener in an amount of 0.5 to 5 weight percent, wherein the conductive paste compound has a viscosity of 2,000 Pa·sec or less and an amount of volatile component is 2.0 weight percent or less.
- 10 2. The conductive paste compound used for filling via holes as in claim 1, further comprising a dispersant in an amount of 0.01 to 1.5 weight percent against 100 weight parts of said components (a) to (c).
3. The compound as in claim 1 or 2, wherein said conductive filler comprises at least one fine grain selected from the group consisting of gold, silver, palladium, copper, nickel, tin, and lead.
- 15 4. The compound as in claims 1, 2 or 3, wherein said conductive filler comprises copper with a surface oxygen concentration of 1.0 weight percent or less.
5. The compound as in any one of claims 1 to 4, wherein said epoxy resin comprises at least one liquid epoxy resin selected from the group consisting of bisphenol A epoxy resin, bisphenol F epoxy resin, alicyclic epoxy resin, amine epoxy resin, and glycidyl esterified epoxy resin.
- 20 6. The compound as in any one of claims 1 to 5, wherein said liquid epoxy resin contains 10 weight percent or more of an epoxy resin which comprises glycidyl esterified dimer acids.
- 25 7. The compound as in any one of claims 1 to 6, wherein said liquid epoxy resin is a compound comprising at least 50 weight percent or less of one epoxy resin selected from the group consisting of bisphenol A and bisphenol F, and further comprising 50 weight percent or more of epoxy resin composed of glycidyl esterified dimer acids with an epoxy equivalent of from 300 to 600 g/eq.
- 30 8. The compound as in any one of claims 1 to 7, wherein said hardener is at least one hardener selected from the group consisting of amine hardeners, urea hardeners, acid anhydride hardeners, and aromatic amine hardeners.
- 35 9. The compound as in any one of claims 1 to 8, wherein said hardener comprises a subclinical hardener.
10. The compound as in any one of claims 2 to 9, wherein said dispersant comprises at least one dispersant selected from the group consisting of nonionic dispersants, anionic dispersants, and a fourth class ammonium salt type cationic dispersant.
- 40 11. A double sided printed circuit board comprising an insulating base material disposed with inner via holes which are filled with a conductive resin compound comprising a conductive filler in an amount of 80 to 92 weight percent having an average particle size of 0.5 to 20 μ m and a specific surface area of 0.1 to 1.5 m²/g, and further comprising an epoxy resin having an epoxy ring-opening in an amount of 4.5 to 20 weight percent, wherein upper and lower electrode layers present on the surface of said insulating base material are electrically connected.
12. The double sided printed circuit board as in claim 11, wherein said insulating base material comprises a composite material of an aramid fiber and a thermosetting resin.
- 50 13. The double sided printed circuit board as in claim 11, wherein said insulating base material comprises a composite material of an aramid nonwoven fabric and an epoxy resin.
14. A multilayer printed circuit board comprising a plurality of insulating base material layers and two or more electrode layers, wherein each insulating base material is disposed with inner via holes filled with a conductive resin compound comprising a conductive filler in an amount of 80 to 92 weight percent having an average particle size of 0.5 to 20 μ m and a specific surface area of 0.1 to 1.5 m²/g, and further comprising an epoxy resin having an epoxy ring-opening in an amount of 4.5 to 20 weight

percent, wherein each electrode layer is electrically connected.

15. The multilayer printed circuit board as in claim 14, wherein said insulating base material comprises a composite material of an aramid fiber and a thermosetting resin.
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16. The multilayer printed circuit board as in claim 14 or 15, wherein said insulating base material comprises a composite material of an aramid nonwoven fabric and an epoxy resin.
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17. A method of manufacturing a double sided printed circuit board comprising the steps of:
filling the via holes with a conductive paste compound comprising (a) a conductive filler in an amount of 80 to 92 weight percent having an average particle size of 0.5 to 20 μ m and a specific surface area of 0.1 to 1.5 m²/g, (b) a liquid epoxy resin in an amount of 4.5 to 20 weight percent containing two or more epoxy groups and having a room temperature viscosity of 15 Pa \cdot sec or less, and (c) a hardener in an amount of 0.5 to 5 weight percent, wherein the conductive paste compound has a viscosity of 2,000 Pa \cdot sec or less and an amount of volatile component of 2.0 weight percent or less;
15 placing said prepreg between copper foils on an upper and lower layer and providing heat and pressurization; and
20 forming circuits by etching the copper foils.
18. The method of manufacturing a double sided printed circuit board as in claim 17, wherein said prepreg comprises a composite material of an aramid fiber and a thermosetting resin.
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19. The method of manufacturing a double sided printed circuit board as in claim 17, wherein said prepreg comprises a sheet composed of an aramid nonwoven fabric impregnated with a thermosetting epoxy resin.
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20. The method as in any one of claims 17 to 19, further comprising a dispersant in an amount of 0.01 to 1.5 weight percent against 100 weight parts of said components (a) to (c).
21. The method as in any one of claims 17 to 20, wherein said conductive filler comprises at least one fine grain selected from the group consisting of gold, silver, palladium, copper, nickel, tin, and lead.
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22. The method as in any one of claims 17 to 21, wherein said conductive filler comprises copper with a surface oxygen concentration of 1.0 weight percent or less.
23. The method as in any one of claims 17 to 22, wherein said epoxy resin comprises at least one liquid epoxy resin selected from the group consisting of bisphenol A epoxy resin, bisphenol F epoxy resin, alicyclic epoxy resin, amine epoxy resin, and glycidyl esterified epoxy resin.
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24. The method as in any one of claims 17 to 23, wherein said liquid epoxy resin contains 10 weight percent or more of an epoxy resin which is composed of glycidyl esterified dimer acids.
25. The method as in any one of claims 17 to 24, wherein said liquid epoxy resin is a compound comprising at least 50 weight percent or less of one epoxy resin selected from the group consisting of bisphenol A and bisphenol F, and further comprising 50 weight percent or more of epoxy resin composed of glycidyl esterified dimer acids with an epoxy equivalent of from 300 to 600 g/eq.
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26. The method as in any one of claims 17 to 25, wherein said hardener is at least one hardener selected from the group consisting of amine hardeners, urea hardeners, acid anhydride hardeners, and aromatic amine hardeners.
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27. A method of manufacturing a multilayer printed circuit board comprising the steps of:
filling the via holes with a conductive paste compound comprising (a) a conductive filler in an amount of 80 to 92 weight percent having an average particle size of 0.5 to 20 μ m and a specific surface area of 0.1 to 1.5 m²/g, (b) a liquid epoxy resin in an amount of 4.5 to 20 weight percent
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containing two or more epoxy groups and having a room temperature viscosity of 15 Pa·sec or less, and (c) a hardener at 0.5 to 5 weight percent, wherein the conductive paste compound has a viscosity of 2,000 Pa·sec or less and an amount of volatile component of 2.0 weight percent or less;

5 positioning said prepreg above and below a double sided printed circuit board;
placing said preprints between copper foils on the top layers, providing heat and pressurization, and etching the copper foils; or
providing heat and pressurization and forming circuits.

28. The method of manufacturing a multilayer printed circuit board as in claim 27, wherein said prepreg 10 comprises a composite material of an aramid fiber and a thermosetting resin.

29. The method of manufacturing a multilayer printed circuit board as in claim 27, wherein said prepreg comprises a sheet composed of an aramid nonwoven fabric impregnated with a thermosetting epoxy resin.

15 30. The method as in claim 27, 28 or 29, further comprising a dispersant in an amount of 0.01 to 1.5 weight percent against 100 weight parts of said components (a) to (c).

31. The method as in any one of claims 27 to 30, wherein said conductive filler comprises at least one fine 20 grain selected from the group consisting of gold, silver, palladium, copper, nickel, tin, and lead.

32. The method as in any one of claims 27 to 31, wherein said conductive filler comprises copper with a surface oxygen concentration of 1.0 weight percent or less.

25 33. The method as in any one of claims 27 to 32, wherein said epoxy resin comprises at least one liquid epoxy resin selected from the group consisting of bisphenol A epoxy resin, bisphenol F epoxy resin, alicyclic epoxy resin, amine epoxy resin, and glycidyl esterified epoxy resin.

34. The method as in any one of claims 27 to 33, wherein said liquid epoxy resin contains 10 weight 30 percent or more of an epoxy resin which is composed of glycidyl esterified dimer acids.

35. The method as in any one of claims 27 to 34, wherein said liquid epoxy resin is a compound comprising at least 50 weight percent or less of one epoxy resin selected from the group consisting of bisphenol A and bisphenol F, and further comprising 50 weight percent or more of epoxy resin composed of glycidyl esterified dimer acids with an epoxy equivalent of from 300 to 600 (g/eq).

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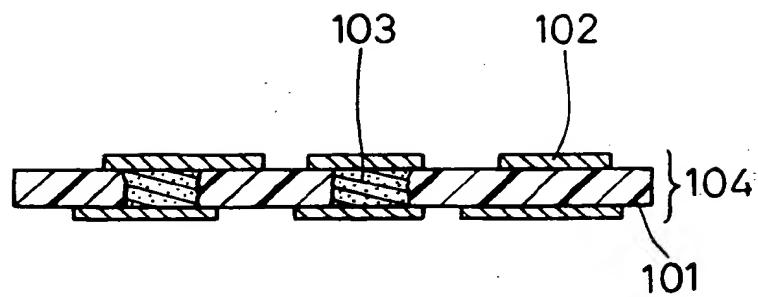
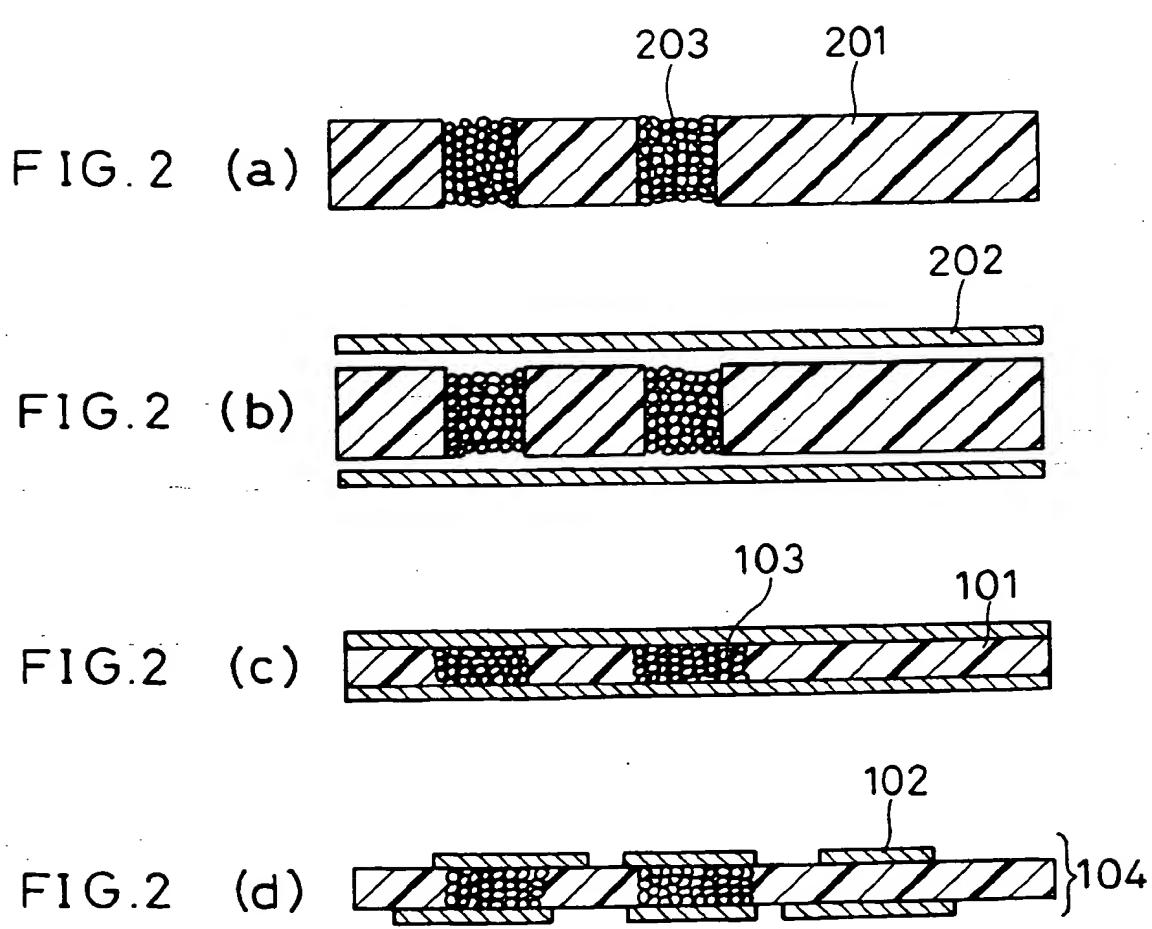


FIG.1



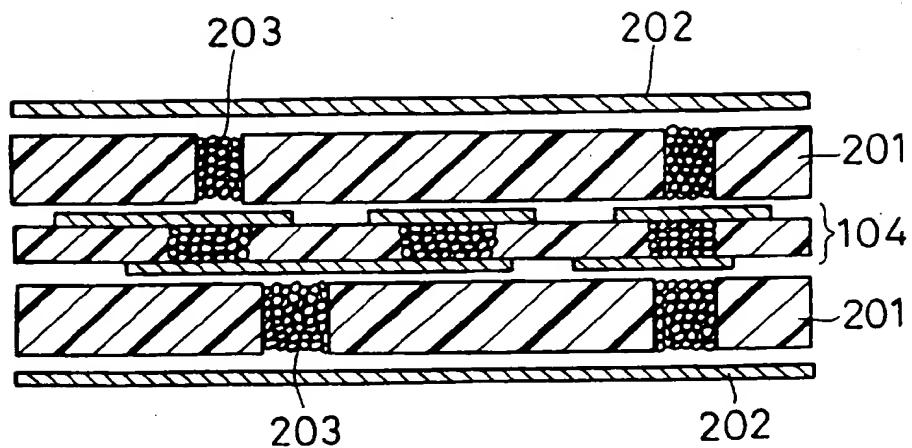


FIG. 3 (a)

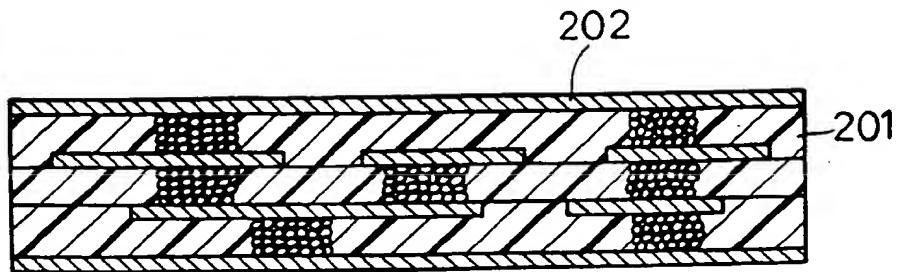


FIG. 3 (b)

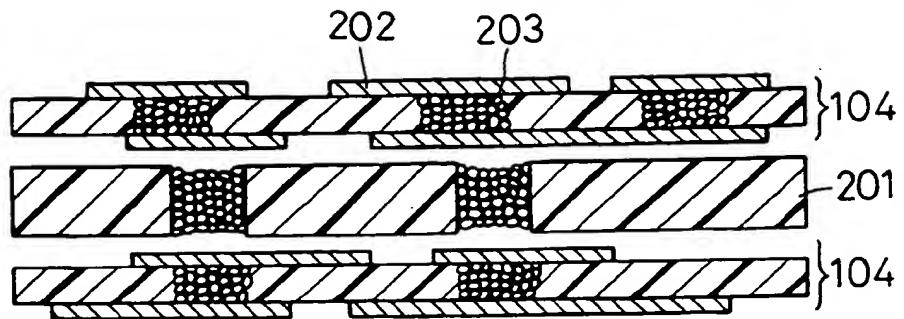


FIG.4 (a)

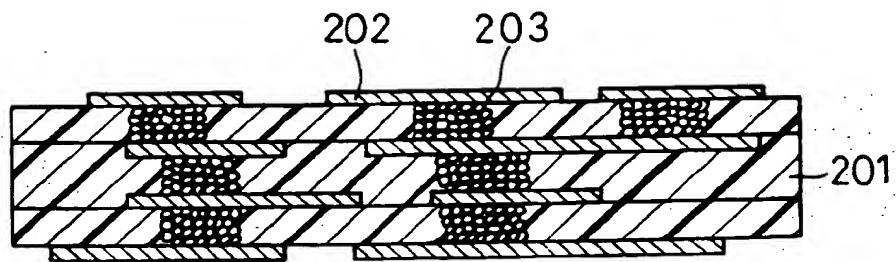


FIG.4 (b)

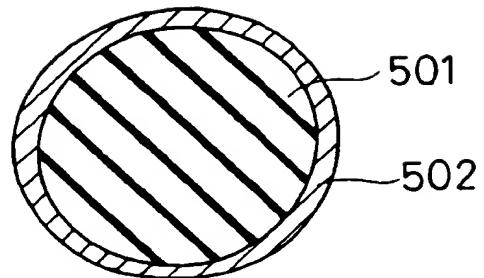


FIG.5

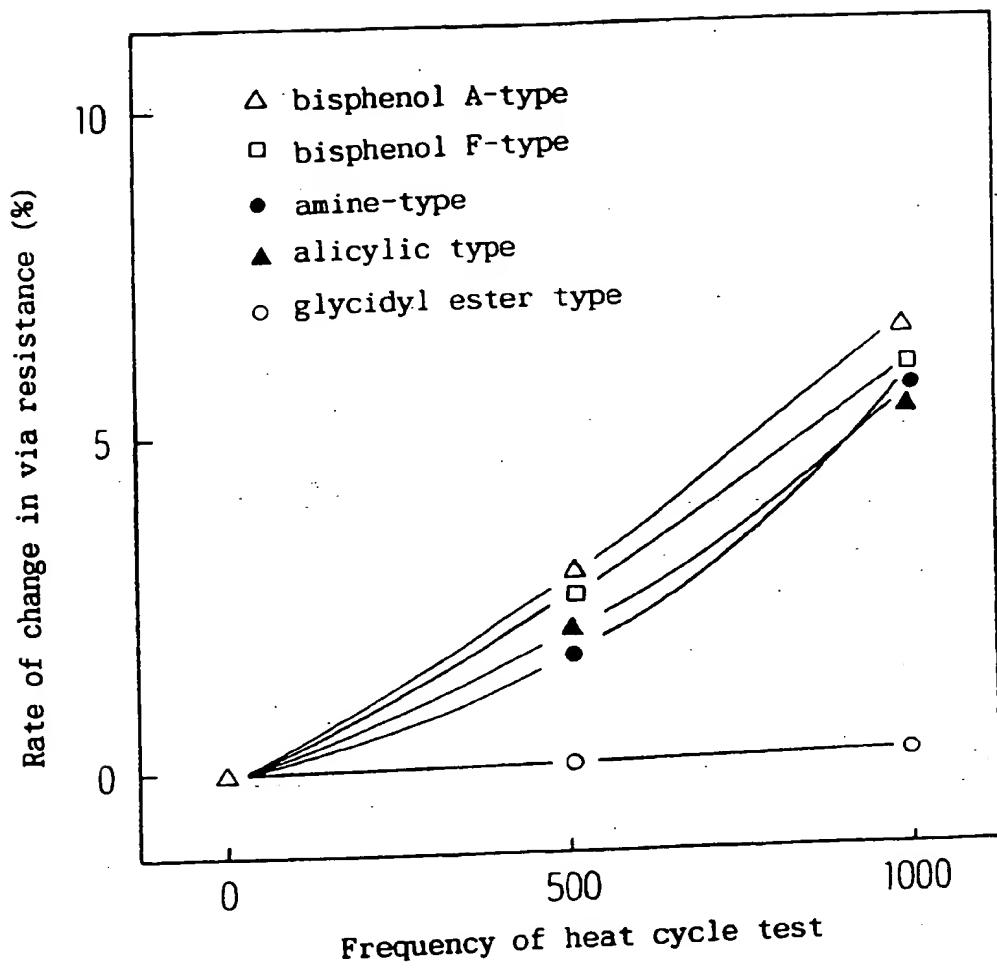


FIG. 6

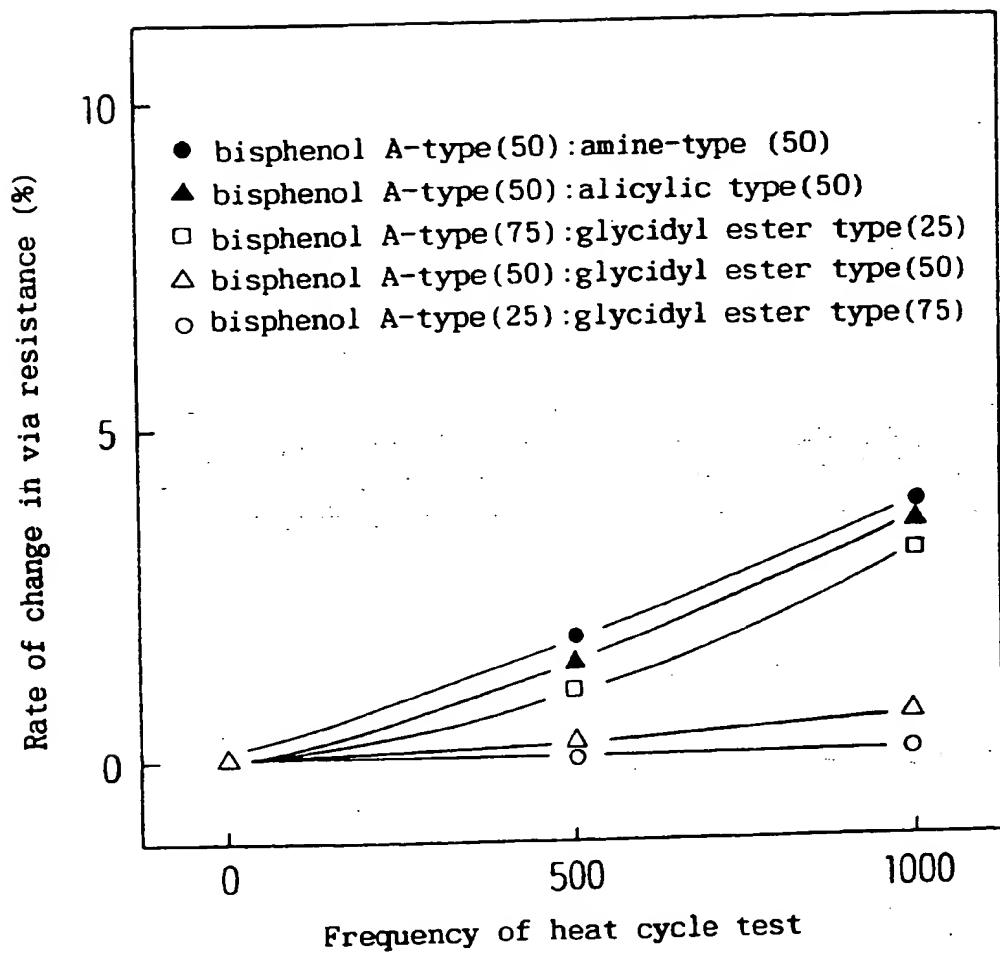


FIG. 7

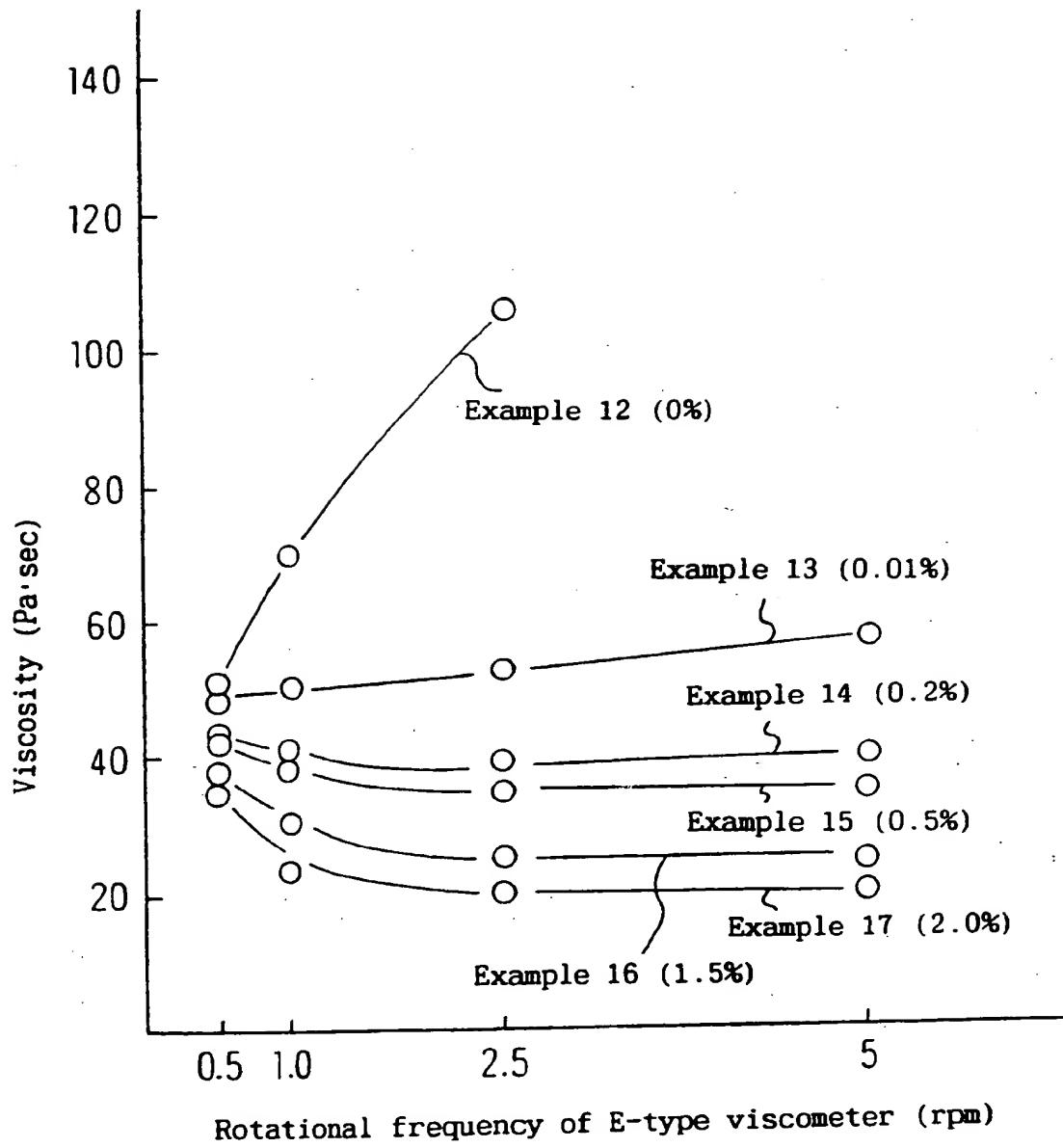


FIG. 8



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 11 7098

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	DE-A-41 25 879 (HITACHI) * column 3, line 16 - line 65 * ---	1, 3, 5	H05K3/40 H05K1/09 H01B1/22
A	US-A-4 967 314 (HIGGINS, III) * column 5, line 25 - line 32 * ---	1, 3, 14, 17, 21	
A	EP-A-0 279 979 (SHELDALH) * claims * ---	1, 3, 5	
A	MICROELECTRONICS JOURNAL, vol. 18, no. 3, May/June 1987, LUTON GB pages 22 - 40 A.K. COUSENS ET AL. 'Polymer thick film systems and surface mount techniques' * page 26 * * page 28, last paragraph * ---	1, 3, 5, 8	
A	US-A-4 383 363 (HAYAKAWA ET AL.) * figures * ---	1, 3, 11	
A	GB-A-974 919 (CHOMERICS) * page 2, line 11 - line 35 * ---	1, 3, 5	
A	PATENT ABSTRACTS OF JAPAN vol. 17, no. 583 (E-1452) 22 October 1993 & JP-A-05 175 650 (TOKUYAMA SODA CO) 13 July 1993 * abstract * -----	1	H05K H01B C09D C08K
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search		Examiner
THE HAGUE	30 January 1995		Mes, L
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